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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

BY CHARLES F. MABERY.

Presented February 8, 1882.

THE investigations described in the following papers were made under my supervision, and they formed a part of the work in the Summer Course of Instruction in Chemistry for 1881.

DIBROMIODACRYLIC AND CHLORBROMIODACRYLIC ACIDS.

CHARLES F. MABERY AND RACHEL LLOYD.

From the ease with which various substituted acrylic acids have been obtained from brompropiolic acid,* we were led to believe that derivatives of some interest would result by the simultaneous addition of different halogens. This idea was confirmed by a few preliminary experiments, which showed that iodine monobromide and iodine monochloride could readily be made to form addition-products with brompropiolic acid. These substances have been submitted to a careful study, and the results we have obtained are presented in this paper.

DIBROMIODACRYLIC ACID.

Dibromiodacrylic acid was made from brompropiolic acid, by the action of iodine monobromide. In the preparation of iodine monobromide according to the method of Lagermarck,† the required weight of iodine, with an excess of bromine, was heated to 50° for ten minutes on the water bath. Dibromiodacrylic acid was formed in small quantity, when the solid residue left by evaporation of the excess of bromine was dissolved in ether and allowed to stand with brompropiolic acid. The product of this reaction, however, consisted to a large extent of an oil, from which very little pure substance could be recovered. This difficulty was partially overcome by the application of heat; and by boiling the solution for an hour on the water bath we succeeded in obtaining about forty per cent of the amount theoretically required. The thick pasty mass left after the evaporation of the ether soon solidified, and was easily purified by crystallization from hot water.

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* These Proceedings, Vol. XVI. pp. 211, 235.

† Berichte der deutsch. chem. Gesellsch. 1874, 907.

Dibromiodacrylic acid dissolves readily in ether, alcohol, carbonic disulphide, and chloroform. In cold water it is rather sparingly soluble; from a concentrated hot solution it falls at first as an oil, which crystallizes as the solution cools, in oblique prisms of the monoclinic system. It melts at 139°–140°, and sublimes slowly at higher temperatures.

The composition of this substance was determined by the following analyses: —

I. 1.0762 grm. of the substance gave 0.3385 grm. CO_2 and 0.0420 grm. H_2O.

II. 0.1993 grm. of the substance gave by the method of Carius 0.3385 grm. Ag Br + Ag I.

	Calculated for $C_3HBr_2IO_2$.	Found.	
		I.	II.
C	10.11	9.85	
H	.28	.43	
2 Br + I	80.63		80.21

To determine the solubility of this acid at ordinary temperatures, we used the method of V. Meyer. The filtered solution was neutralized with baric carbonate, and the barium estimated by precipitation with sulphuric acid.

I. 8.7164 grms. solution gave 0.0968 grm. $BaSO_4$.

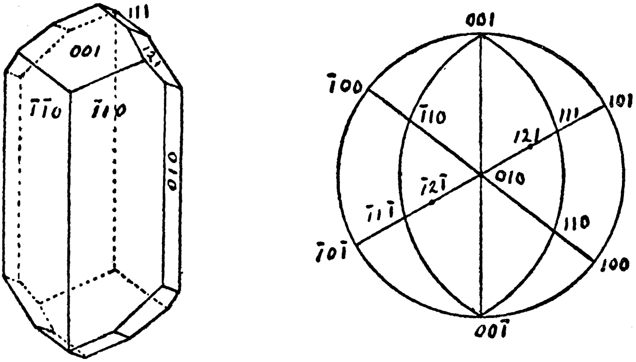
II. 9.7772 grms. solution gave 0.1089 grm. $BaSO_4$.

The solution saturated at 20° contains, therefore, the percentages: —

I.	II.
3.39	3.40

Dr. W. H. Melville has made a crystallographic examination of this substance, and obtained the following results: —

CRYSTALLINE FORM OF DIBROMIODACRYLIC ACID.



MONOCLINIC SYSTEM.

Forms {001}, {010}, {110}, {121}, {111}.*

Elements: — Clinodiagonal, $a = 0.617$
Orthodiagonal, $b = 1.$
Vertical Axis, $c = 0.581$
Angle of Axes = 52° 11½′

				Observed.	Calculated.
Angles between normals	001	and	110	123° 26′	Fundamental angles
	110	"	010	64°	
	111	"	110	59° 14′½	
	111	"	010	62° 11′	61° 47′
	121	"	010	42° 59′	42° 58′
	121	"	001	70° 29′	70° 19′
	121	"	110	55° 59′	56° 13′
	121	"	$\bar{1}10$	84° 55′	85° 5′½

The following salts of this acid have been examined: —

Baric dibromiodacrylate $Ba(C_3Br_2IO_2)_2 . 3\frac{1}{2}H_2O$.

To prepare the barium salt, a solution of the acid was neutralized with baric carbonate and the filtered solution concentrated by evaporation. On cooling the salt crystallized in rhombic prisms, which were very soluble in hot, less soluble in cold water. The air-dried salt lost three and a half molecules of crystal water at 80°.

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* The form {111} appeared only on a few crystals.

I. 0.7087 grm. of the air-dried salt lost 0.0512 grm. H_2O at 80°.
II. 0.7273 grm. of the salt lost 0.0535 grm. H_2O at 80°.
III. 0.6244 grm. of the salt lost 0.0441 grm. H_2O at 80°.
IV. 0.6575 grm. of the anhydrous salt gave 0.1808 grm. Ba SO_4.

	Calculated for $Ba(C_3Br_2IO_2)_2 . 3\frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
H_2O	6.92	7.23	7.36	7.06

	Calculated for $Ba(C_3Br_2IO_2)_2$.	Found.
Ba	16.17	16.16

The solubility of this salt in cold water was determined by V. Meyer's method. The saturated solution was filtered, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 2.6342 grms. of a solution saturated at 20° gave 0.1038 grm. $BaSO_4$.
II. 2.0175 grms. of a solution saturated at 20° gave 0.0806 grm. $BaSO_4$.

From these determinations the following percentages were calculated: —

I.	II.
14.32	14.52

Calcic dibromiodacrylate $Ca(C_3Br_2IO_2)_2$.

The calcium salt was made by saturating an aqueous solution of the acid with calcic carbonate. From the concentrated solution the salt crystallized in clustered needles which were less soluble in cold than in hot water. When air-dried it was constant at 80°.

0.4118 grm. of the salt dried at 80° gave 0.0714 grm. $CaSO_4$.

	Calculated for $Ca(C_3Br_2IO_2)_2$.	Found.
Ca	5.33	5.10

Potassic dibromiodacrylate $KC_3Br_2IO_2$?

This salt was prepared by neutralizing an aqueous solution of the acid with potassic carbonate and evaporating on the water bath. It separated in the form of rhombic plates, which proved to be so deliquescent that we were unable to determine the water of crystallization.

0.8834 grm. of the salt dried at 80° gave 0.1842 grm. K_2SO_4.

	Calculated for $KC_3Br_2IO_2$.	Found.
K	9.92	9.92

Argentic dibromiodacrylate $AgC_3Br_2IO_2$.

From a hot aqueous solution of the acid the silver salt is precipitated by the addition of argentic nitrate in hexagonal plates. It may be recrystallized from hot water without decomposition, and it is but slightly affected by the action of light. The salt was dried over sulphuric acid for analysis.

1.0737 grm. of the salt gave by precipitation with HBr 0.4288 grm. AgBr.

	Calculated for $AgC_3Br_2IO_2$.	Found.
Ag	23.32	22.98

When dibromiodacrylic acid is heated to 100° in a closed tube with bromine, iodine is set free and bromine takes its place. The substance thus formed is identical with the tribromacrylic acid described by Professor H. B. Hill and one of us * as shown by its melting point 115–118°, and by a study of its crystalline form. The following angles were measured by Dr. Melville: —

	Angles between normals.	Tribromacrylic acid from dibromiodacrylic.	Tribromacrylic acid from brompropiolic.
Zone [010, 110]	110 and 010	65° 33′	65° 38′
	010 “ $\bar{1}10$	65° 44	
	$\bar{1}10$ “ $\bar{1}\bar{1}0$	48° 28′	48° 40′
	$\bar{1}\bar{1}0$ “ $0\bar{1}0$	65° 52½′	
	$0\bar{1}0$ “ $1\bar{1}0$	65° 35′	
	$1\bar{1}0$ “ 110	48° 44′	
		359° 56½′	
Zone [010, 011]	010 and 011	63° 11′	63° 14′
	011 “ $0\bar{1}1$	54° 5′	53° 33′
	$0\bar{1}1$ “ $0\bar{1}0$	62° 56′	

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* These Proceedings, Vol. XVI. p. 216.

It also gave the percentage of bromine required for tribromacrylic acid.

0.1553 grm. substance gave 0.2819 grm. AgBr.

	Calculated for $C_3HBr_3O_2$.	Found.
Br	77.66	77.25

CHLORBROMIODACRYLIC ACID.

Chlorbromiodacrylic acid may be prepared most conveniently by heating brompropiolic acid with an ethereal solution of iodine monochloride, although without the application of heat the reaction takes place slowly. Iodine monochloride was made according to the method proposed by Bunsen.* The calculated weight of iodine was dissolved in aqua regia with the aid of heat, and after cooling the solution was extracted with ether and washed thoroughly with water. When brompropiolic acid is heated for an hour with this solution, the oily liquid left on evaporation of the ether soon deposits large prismatic crystals of the addition-product. For purification the crude product was pressed in filter paper and recrystallized from hot water.

This substance is readily soluble in ether and alcohol, somewhat less so in carbonic disulphide and chloroform. From a hot aqueous solution it separates as an oil which crystallizes on cooling in rhombic prisms of the monoclinic system. By crystallization from water we did not succeed in raising the melting point above 110°; but the crystals formed by slow evaporation of a solution in carbonic disulphide melted at 115–116°. It sublimes freely at somewhat higher temperatures.

This acid was identified by the following analyses:—

I. 0.6743 grm. substance gave 0.2843 grm. CO_2.†

II. 0.1505 grm. substance gave 0.2721 grm. AgCl + AgBr + AgI.

	Calculated for $C_3HClBrIO_2$.	Found.	
		I.	II.
C	11.55	11.50	
H	.32		
Cl + Br + I	77.84		77.41

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* Ann. Chem. u. Pharm. LXXIV. 8.

† By an accident the water in this combustion was lost.

The following results were obtained in determining the solubility in cold water: —

I. 8.1470 grms. of a solution saturated at 20° gave 0.1396 grm. $BaSO_4$.

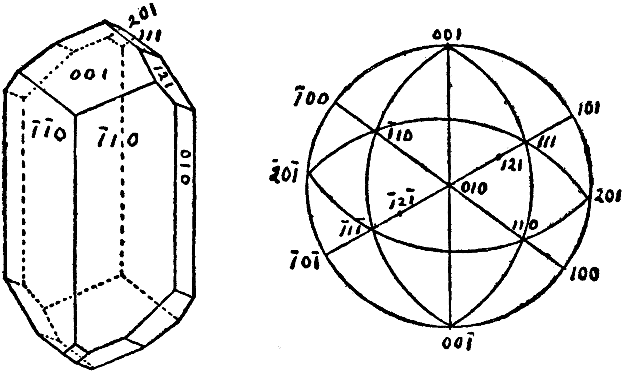
II. 5.4630 grms. of a solution saturated at 20° gave 0.0968 grm. $BaSO_4$.

From these results were calculated the percentages: —

I.	II.
4.58	4.74

For a determination of the crystalline form of this acid we are indebted to the kindness of Dr. Melville, who obtained the following results: —

CRYSTALLINE FORM OF CHLORBROMIODACRYLIC ACID.



MONOCLINIC SYSTEM.

Forms {001}, {010}, {110}, {121}, {111}, {201},

Elements: — Clinodiagonal, $a = 0.594$
Orthodiagonal, $b = 1.$
Vertical Axis, $c = 0.572$
Angle of axes $XZ = 52° 47'$

				Observed.	Calculated.
Angles between normals	111	and	110	58° 23′	Fundamental Angles.
	121	"	110	55° 45′	
	121	"	010	43° 48′	
	111	"	010	62° 43′	62° 28′
	110	"	001	123° 26′	123° 13′
	110	"	010	65° 3′	64° 56′
	111	"	11̄0	82° 24′	82° 23′

It will be seen by inspection of the forms of dibromiodacrylic and chlorbromiodacrylic acids that these substances present a striking instance of isomorphism. In fact the only form not common to both is that of {201}, which was not observed on the crystals of dibromiodacrylic acid. This similarity in form, which extends also to tribromacrylic acid, is rendered more prominent by a comparison of the observed angles. The measurements of tribromacrylic acid show a greater variation in the observed angles except in the case of the angle which the prism {110} makes with the pinacoid {010}.

	Dibromiod-acrylic acid.	Chlorbromiod-acrylic acid.	Tribrom-acrylic acid.
110 and 010	64°	65° 3′	65°33
110 " $\bar{1}$10	128°	130° 6′	
110 " 001	123° 26′	123° 26′	
111 " 010	62° 11′	62° 43′	
111 " 110	59° 14½′	58° 23′	
121 " 010	42° 59′	43° 48′	
121 " 110	55° 59′	55° 45′	

The elements of the crystals also proved to be nearly identical.

	Dibromiod-acrylic acid.	Chlorbromiod-acrylic acid.
Clinodiagonal *a*	0.617	0.594
Orthodiagonal *b*	1.	1.
Vertical axis *c*	0.581	0.572
Angle of axes XZ	52° 11′½	52° 47′

A study was made of some of the more important salts of chlorbromiodacrylic acid.

Baric chlorbromiodacrylate $Ba(C_3ClBrIO_2)_2 \cdot 3\frac{1}{2}H_2O$.

A solution of the acid was saturated with baric carbonate, filtered, and concentrated on the water bath. The salt separated on cooling in rectangular prisms, which when dried by exposure to the air contained three and a half molecules of crystal water. It is quite soluble in cold, and very soluble in hot water.

I. 0.8250 grm. of the air-dried salt lost when heated to 80° 0.0636 grm. H_2O.
II. 0.7273 grm. of the air-dried salt lost at 80° 0.0540 grm. H_2O.
III. 0.5401 grm. of the air-dried salt lost at 80° 0.0384 grm. H_2O.
IV. 0.5502 grm. of the air-dried salt lost at 80° 0.0438 grm. H_2O.

V. 0.6697 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2080 grm. $BaSO_4$.
VI. 0.5032 grm. of the anhydrous salt gave 0.1570 grm. $BaSO_4$.
VII. 0.4959 grm. of the anhydrous salt gave 0.1527 grm. $BaSO_4$.

	Calculated for $Ba(C_3ClBrIO_2)_2 . 3\frac{1}{2}H_2O$.	Found.			
		I.	II.	III.	IV.
H_2O	7.67	7.71	7.44	7.11	7.96

	Calculated for $Ba(C_3ClBrIO_2)_2$	Found.		
		V.	VI.	VII.
Ba	18.07	18.26	18.34	18.10

The solubility at 20° was determined by evaporating a saturated solution to dryness and igniting the residue with sulphuric acid.

I. 3.7500 grms. solution gave 0.2339 grm. $BaSO_4$.
II. 3.1458 grms. solution gave 0.1957 grm. $BaSO_4$.

According to these determinations a solution saturated at 20° contains the percentages: —

I.	II.
20.30	20.23

Calcic chlorbromiodacrylate $Ca(C_3ClBrIO_2)_2 . H_2O$.

When a solution of the acid is neutralized with calcic carbonate, and the filtered solution concentrated by evaporation, the calcium salt separates in the form of branching needles. The air-dried salt contains one molecule of crystal water, which it loses at 80°.

I. 0.7180 grm. of the air-dried salt lost 0.0216 grm. H_2O at 80°.
II. 0.6770 grm. of the air-dried salt lost 0.0197 grm. H_2O at 80°.
III. 0.6583 grm. of the anhydrous salt gave 0.1404 grm. $CaSO_4$.

	Calculated for $Ca(C_3ClBrIO_2)_2 . H_2O$.	Found.	
		I.	II.
H_2O	2.66	3.01	291

	Calculated for $Ca(C_3ClBrIO_2)_2$.	Found.
		III.
Ca	6.05	6.27

Potassic chlorbromiodacrylate $KC_3ClBrIO_2$?

The potassium salt is obtained as a very deliquescent solid mass by evaporating a solution of the acid after neutralizing with potassic carbonate.

0.8076 grm. of the salt dried at 80° gave on ignition with H_2SO_4 0.2176 grm. K_2SO_4.

	Calculated for $KC_3ClBrIO_2$.	Found.
K	11.19	11.27

Argentic chlorbromiodacrylate $AgC_3ClBrIO_2$.

The silver salt was prepared by the addition of argentic nitrate to a hot aqueous solution of the acid. It crystallizes in rhombic prisms, which are quite soluble in hot, sparingly soluble in cold water.

I. 0.5383 grm. of the salt gave 0.1825 grm. AgCl.
II. 0.5129 grm. of the salt gave 0.1766 grm. AgCl.

	Calculated for $AgC_3ClBrIO_2$.	Found.	
		I.	II.
Ag	25.80	25.52	25.91

PRELIMINARY NOTICE ON ORTHOIODBENZYLBROMIDE AND ITS DERIVATIVES.*

Charles F. Mabery and Franklin C. Robinson.

Orthoiodbenzylbromide is formed when bromine is allowed to act on orthoiodtoluol at temperatures near its boiling point. In the preparation of orthoiodtoluol we obtained the most satisfactory results from the sulphate of orthodiazotoluol. Orthotoluidin from the factory of Kahlbaum at Berlin was treated in quantities of 10 grms. each with two molecules of sulphuric acid, and to this mixture, kept cold with snow, was added gradually a solution of one molecule of sodic nitrite. On the addition of hydriodic acid (boiling point ·127°) in slight excess over the calculated amount for the solution of the diazo-compound thus obtained, orthoiodtoluol was precipated as a heavy oily liquid.

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* Since Professor Jackson decided not to include orthoiodbenzylbromide in his researches on the substituted benzyl compounds, we have undertaken its study. (C. F. M.)

The crude product was washed with sodic hydrate and acetic acid, and lastly with water. It was then dried over calcic chloride, and finally purified by fractional distillation. In this way from 20 grms. orthotoluidin we obtained before fractioning 28 grms. orthoiodtoluol, which gave 20 grms. boiling at 211° (mercury column wholly in vapor).*

To convert orthoiodtoluol into orthoiodbenzylbromide, 10 grms. were heated to 190–200° under a return condenser, and 10 grms. bromine allowed to run into the flask from a drop funnel as rapidly as it was absorbed. On cooling, the product of the reaction formed a thick oily liquid which did not solidify at 0°. It was therefore washed with a dilute solution of sodic hydrate, to remove the iodine which was invariably set free during the bromiring, and distilled in the vapor of concentrated hydrobromic acid according to the method followed by Professor Jackson in the purification of orthobrombenzylbromide.† The distillate solidified when cooled with snow, and after removing the oil by pressure in filter paper, it was purified by crystallization from ligroin.

The composition of this substance was established by the following analyses: —

I. 0.1994 grm. of the substance gave 0.3945 grm. Ag Br + Ag I.
II. 0.2793 grm. of the substance gave 0.3945 grm. Ag Br + Ag I.
III. 0.3246 grm. of the substance gave 0.3350 grm. CO_2 and 0.0674 grm. H_2O.

Calculated for C_7H_6BrI.		Found.		
		I.	II.	III.
C	28.28			28.16
H	2.02			2.30
Br + I	69.68	69.53	69.11	

Orthoiodbenzylbromide is readily soluble in ether, hot alcohol, benzol, carbonic disulphide, and chloroform. It is nearly, if not quite, insoluble in water, and very sparingly soluble in cold ligroin. From a cold saturated solution in ligroin it crystallizes in flattened prisms often 2 or 3 centimeters in length. When crystallization takes place from a hot solution it appears in the form of short thick prisms. The vapor of this substance affects the mucous membrane in the same way as that of all the benzyl compounds thus far examined, and it seems to be far more volatile than the corresponding para compound. It melts at 52–53°, and at higher temperatures sublimes slowly in oily drops which soon solidify in radiating needles. By oxidation with dilute nitric acid it is converted into an acid which melts at 150–155°. Since the orthoiodbenzoic acid obtained by Kekulé* from orthoiodtoluol melted at 155–156°, our product without doubt has the same composition.

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* Kekulé, Berichte der deutsch. chem. Gesellsch. 1874, 1007.

† These Proceedings, Vol. XII. p. 217.

As a further proof of the constitution of orthoiodbenzylbromide we made the nitril, and from it orthoiodalphatoluic acid. To form the nitril the bromide was boiled with an alcoholic solution of potassic cyanide. The oily liquid precipitated by the addition of water was heated to 125° for four hours with fuming hydrochloric acid. When cold the oil solidified, and more of the acid separated from the solution in long needles. After removing the excess of hydrochloric acid, the crude product was purified by crystallization from hot water.

Orthoiodalphatoluic acid crystallizes in fine felted needles which are sparingly soluble in cold, readily soluble in hot water and in alcohol, ether, carbonic disulphide, and ligroin. With the limited amount of material at our disposal we were unable to raise the melting point above 95–96°. It would seem, however, from the analogy of the orthobromalphatoluic acid that the melting point of our acid should be somewhat higher. When we return to this subject and have access to a larger supply of the acid, its melting point will be more carefully tested. The silver salt of this acid was made by adding argentic nitrate to an aqueous solution of the ammonium salt. It separated from the solution as a curdy precipitate which was but slightly soluble in water, readily soluble in dilute nitric acid. For analysis it was dried over sulphuric acid.

0.2615 grm. of the salt gave by precipitation with HCl 0.1008 grm. AgCl.

	Calculated for $C_7H_6ICOOAg$.	Found.
Ag	29.27	29.00

We also submitted the bromide to the action of alchoholic ammonia; but as the result of one experiment with a small quantity of substance we succeeded in isolating only the primary amine. The product of this reaction was treated with water, and the aqueous solution evaporated on the water bath. Upon the addition of sodic hydrate the free base was partially precipitated as an oily liquid, and more of the oil was obtained by extracting the solution with ether. The residue left by evaporation of the ether was immediately converted into the carbonate by absorbing carbonic dioxide from the air. It was dissolved in alcohol, a little hydrochloric acid added, and the platinum salt formed by the addition of chlorplatinic acid. This salt crystallized in pale yellow microscopic prisms, which were sparingly soluble in water and cold alcohol, readily in hot, and insoluble in ether. It was purified by recrystallization from hot alcohol, washed with ether, and dried over sulphuric acid for analysis.

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* Berichte der deutsch. chem. Gesellsch. 1874, 1007.

0.2082 grm. of the salt gave on ignition 0.0468 grm. platinum.

	Calculated for $(C_7H_6INH_3)_2PtCl_6$.	Found.
Pt	22.48	22.48

Since our work was interrupted by the closing of the summer term, a more complete examination of the derivatives of orthoiodbenzylbromide must be reserved for another paper.

CHLORTRIBROMPROPIONIC ACID.

CHARLES F. MABERY AND H. C. WEBER.

The formation of chlortribrompropionic acid by the action of bromine on chlorbromacrylic acid has been mentioned in a previous paper by R. Lloyd and one of us.* Although this reaction took place without difficulty in a chloroform solution at ordinary temperatures, the product proved to consist in great part of an oil which could not be made to crystallize. With the hope of obtaining a more satisfactory yield we tried the action of undiluted bromine at a higher temperature. Chlorbromacrylic acid, melting point 68–70°, with a slight excess over the calculated weight of bromine, was heated to 100° for two hours in a closed tube. The excess of bromine was removed by spontaneous evaporation from the product, which was purified by pressure between folds of filter paper and crystallization from carbonic disulphide. By this method from 6.5 grms. chlorbromacrylic acid we obtained 8.5 grms. essentially pure chlortribrompropionic acid, or about seventy per cent of the theoretical amount.

This acid is readily soluble in ether and alcohol, less soluble in cold than in hot carbonic disulphide and chloroform. In contact with water it forms an oil which does not solidify at 0°. From carbonic disulphide or chloroform it crystallizes by slow evaporation in oblique prisms of the triclinic system which melt at 102–103°. In the analysis of this substance the following results were obtained: —

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* These Proceedings, Vol. XVI. p. 240.

I. 0.1582 grm. of the substance gave by the method of Carius, 0.3234 grm. $AgCl + AgBr$.
II. 0.1582 grm. of the substance gave 0.3251 grm. $AgCl + AgBr$.
III. 0.9373 grm. of the substance gave 1.9049 grm. $AgCl + AgBr$. 1.9003 grm. $AgCl + AgBr$ gave 1.1568 grm. Ag.*
IV. 0.8096 grm. of the substance gave 0.3065 grm. CO_2 and 0.0631 grm. H_2O.

	Calculated for $C_3H_2ClBr_3O_2$.		Found.				
			I.	II.	III.		IV.
C	10.42						10.32
H	.58						.87
Cl + 3 Br	79.75		79.58	80.00			
Cl	10.28	79.75			9.62	79.36	
Br	69.47				69.74		

The barium, calcium, and potassium salts of this acid were made and analyzed.

Baric chlortribrompropionate $Ba(C_3HClBr_3O_2)_2$.

To form the barium salt a solution of the acid was neutralized with baric carbonate and baric hydrate, filtered, and concentrated by spontaneous evaporation at the ordinary temperature. The salt crystallized in slender oblique prisms which were quite soluble in cold water. The air-dried salt was constant when heated to 80°.

I. 0.6933 grm. of the salt dried at 80° gave on ignition with H_2SO_4 0.1920 grm. $BaSO_4$.
II. 0.6440 grm. of the salt dried at 80° gave 0.1793 grm. $BaSO_4$.

	Calculated for $Ba(C_3HClBr_3O_2)_2$.	Found.	
		I.	II.
Ba	16.59	16.26	16.37

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* This determination was made with the aid of the excellent method devised by Mr. L. P. Kinnicutt. (These Proceedings, Vol. XVI. p. 91.)

The solubility of this salt we determined by the method of V. Meyer. A saturated solution was kept at 20° for three hours, filtered, evaporated to dryness, and the residue ignited with sulphuric acid.

I. 1.8400 grm. solution gave 0.0977 grm. $BaSO_4$.
II. 0.8926 grm. solution gave 0.0470 grm. $BaSO_4$.

These results correspond to the percentages: —

I.	II.
18.82	18.66

Calcic chlortribrompropionate $Ca(C_3HClBr_3O_2)_2$.

To prepare the calcium salt we neutralized a solution of the acid with calcic carbonate and calcic hydrate, and allowed the filtered solution to evaporate spontaneously. From the concentrated solution the salt separated in clustered needles, which, when air-dried, were constant at 80°.

1.0691 grm. of the salt dried at 80° gave on ignition with H_2SO_4 0.1883 grm. $CaSO_4$.

	Calculated for $Ca(C_3HClBr_3O_2)_2$.	Found.
Ca	5.49	5.25

Potassic chlortribrompropionate $KC_3HClBr_3O_2 . H_2O$.

The potassium salt was made by neutralizing a solution of the acid with potassic carbonate and evaporating at the ordinary temperature. This salt crystallized in rhombic prisms which are freely soluble in cold water. It contained one molecule of crystal water which was given up over sulphuric acid.

I. 1.0688 grm. air-dried salt gave 0.0502 grm. H_2O.
II. 1.0428 grm. air-dried salt gave 0.0490 grm. H_2O.
III. 0.9802 grm. of the anhydrous salt gave 0.2201 grm. K_2SO_4.

	Calculated for $KC_3HClBr_3O_2 . H_2O$.	Found.	
		I.	II.
H_2O	4.48	4.70	4.72

	Calculated for $KC_3HClBr_3O_2$	Found.
		III.
K	10.20	10.08

The silver salt of this acid proved to be so unstable that we did not succeed in preparing it in a form sufficiently pure for analysis. On the addition of argentic nitrate to an aqueous solution of the acid, even in the cold it immediately became turbid from the separation of argentic chloride.

Although the barium salt is comparatively stable, we found that it was slowly decomposed when heated in aqueous solution. In order to identify the products of this decomposition, the acid was distilled with an excess of baric hydrate. The distillate was caught in bromine water, the excess of bromine allowed to evaporate, and the solution extracted with ether. The oily residue left by evaporation of the ether solidified at 0°, and possessed an odor characteristic of the substituted ethans. It would seem probable, therefore, that the volatile product of this decomposition was tribromethylen; but it was formed in such small quantity that further study was rendered extremely difficult. The residue in the retort contained baric chloride in abundance, but it gave no reaction for baric bromide. The formation of tribromacrylic acid is thus rendered extremely probable; but the residue unfortunately was lost before it could be subjected to a more critical examination. Since the summer term soon after closed, we were unable to repeat our work, and it must therefore be reserved for future study.

Chlorbromacrylic acid forms also an addition-product with hydrobromic acid. When it is heated to 100° in a closed tube with concentrated hydrobromic acid, an acid is formed which melts at 80°. Further study of this substance, which is probably chlordibrompropionic acid, will be postponed for the present.